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13. SUPPLEMENTARY NOTES

14. ABSTRACT

The report covers work carried out by students at the University of Strathclyde evaluating the application of the dielectric technique to the characterisation of ageing in adhesive bonded structures. The work covers studies of aluminium-epoxy-aluminium and carbon fibre-epoxy-carbon fibre. The ageing in these structures was induced by exposing samples to high humidity and elevated temperatures and revealed the possible correlations between the changes in dielectric property and changes in mechanical property in the joints. This study has established the potential of applying the dielectric technique for the non-destructive analysis of adhesive bonded structures.

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d. Net outlays *(line a, less the sum of lines b and c)*			
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e. Third party (in-kind) contributions			
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h. All other recipient outlays not shown on lines e, f, or g			
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k. Total unliquidated obligations			
l. Recipient's share of unliquidated obligations			
m. Federal share of unliquidated obligations			
n. Total federal share *(sum of lines j and m)*			
o. Total federal funds authorized for this funding period			
p. Unobligated balance of federal funds *(Line o minus line n)*			
Program income, consisting of:			
q. Disbursed program income shown on lines c and/or g above			
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Signature of Authorized Certifying Official G M Mill	Date Report Submitted 23/3/01.

Final Report for AFOSR Contract F49620-1-0530

Development of a Dielectric Based Non-Destructive Examination Method for Adhesive Bonded Structures: A Fundamental Study

Introduction

The project assesses the potential of the dielectric technique to access the processes that occur within adhesive bonded structures during the process of ageing in aggressive environments. Previous studies (see Appendix), have established that it is possible to obtain dielectric frequency and time domain data from adhesive bonded structures. The typical adhesive bond is ideal for such studies being two electrodes- the adherents, sandwiching a dielectric – the adhesive. The aluminium is a good conductor and the adhesive used in most joints – an epoxy resin is a good insulator. Such a structure behaves as a simple capacitor for low frequency dielectric measurements but becomes a transmission line when high frequency observations are made. A previous student has explored the effects of changes in the width of the adhesive bond and the thickness of the adhesive layer on the transmission line characteristics. A simple transmission line theory was found to be capable of quantitatively describing the data obtained and allowed the dielectric permittivity and dielectric loss to be extracted from the frequency dependence of the reflection coefficient data. Transformation of the data into the time domain allowed the reflection coefficient to be determined as a function of time and hence distance along the joint structure. Using this approach it has been possible to identify using idealised structures a number of features; air voids, changes in the adhesive cross section along the joint structure, changes in the degree of cure and changes in the width of the joint with distance. These preliminary studies established the potential of the method for characterising adhesive bonded structures but did not indicate whether it would be possible to use the technique to follow the changes which occur within the joint structure on ageing.

As a consequence of previous involvement in the characterisation of cure using dielectric techniques the question had been posed; 'Can dielectric measurements provide information on the hydration processes accompanying exposure to water of epoxy resins and related materials?'. Studies had been carried out over a number of years on the effects of changes in the chemical structure of the resin, degree and temperature of cure on the rate and nature of the water absorption process. These studies showed that absorbed water is produces relaxations distributed over a broad frequency range which for typical epoxy resins extend between approximately 1 kHz and 12 GHz. The relaxation detected in the 12GHz region is close to that observed for pure water and is attributed to clusters of water molecules located in micro-voids within the matrix. A relaxation is observed in the dry cured resin at approximately 10 kHz and this is associated with relaxation of the hydroxyl dipole created by opening of the epoxy ring. Exposure of a resin to water leads to increases in the dielectric loss across this band of frequencies and the distribution of the loss is a reflection of the type of environment occupied by these water molecules. Increases of dielectric loss in the lower frequency region can be associated with water molecules that are interacting with the pendant hydroxyl groups by hydrogen bonding.

The water molecules that relax in this region are designated – 'bound' water molecules whereas those that relax at approximately 12 GHz are designated 'free' molecules. Water molecules exhibit dielectric relaxation features between these two

extreme situations and the distribution of relaxation processes reflects the extent to which the matrix interacts with the water molecules. The distribution of the water in the matrix has been found to depend on the chemistry of the epoxy resin used, the temperature at which the resin was cured and the proportions of the components used in the resin matrix formulation.

A further question that was raised by the initial studies was whether changes in the surface oxide layer could be detected by dielectric measurements. In order to be able to identify the dielectric signature a study was carried out on the hydration of gamma alumina. It was observed that the dielectric constant of the dry material was frequency independent and the corresponding dielectric loss essentially equal to zero. On hydration surface dipoles are created associated by the formation of hydroxyl groups. The magnitude of the dielectric feature associated with this relaxation grows with the time of exposure. The relaxation frequency for the process is located at approximately 1 MHz and is clear of the relaxation associated with the pendant hydroxyl group attached top the polymer. It was also found that the relaxation does not depend on the type of hydrate that is formed.

It was therefore demonstrated at the beginning of this study that dielectric measurements have the capability of identifying the following processes:-

1) the ingress and distribution of moisture both in terms of type and location in the joint structure.
2) The conversion of oxide to hydroxide (CORROSION) in the interfacial region.

Ageing of a joint lead to a loss of mechanical strength which is a consequence of changes in the physical properties of the adhesive and also changes in the strength of the polymer adherent interface region. Plasticisation as a consequence of moisture ingress and changes of the structure of the oxide interface all contributes to the loss of mechanical strength. The objective of this project were to:-

1) To explore whether any form of a connection might exist between the changes in the mechanical strength of the joint and the changes in the dielectric response of the joint for aluminium –epoxy –aluminium joints.
2) To explore whether the approach used for aluminium –epoxy –aluminium bonded structures might be also used for carbon fibre reinforced plastic (CFRP) jointed structures.
3) To explore whether an approach might be developed for the study of boron fibre patches attached to an aluminium substrate. The latter represents a new challenge as boron fibres are non-conductive and hence may not be used as conductors to define the bonded structures.

Funding was provided through the AFOSR grant for support of a research student for three years, additional support for a research student sponsored by the UK, Engineering and Physical Science Research Council (EPSRC). A post-doctoral worker was also support for a period of three months to undertake the initial evaluation of the boron fibre problem. The EPSRC funded student was able to contribute to the programme and the support received allowed him to visit the USA. The project was operated in collaboration with Dr Robert L. Crane of the Materials Laboratory at the Wright Patterson Air Force Materials Laboratory, Dayton Ohio. The research programme extended over a period of three and a half years and terminated in December 2000. Both students spent periods of time with Dr Crane and were able to provide advice on parallel experiments carried out there and also use the C scan ultrasonic imaging to inspect the state of the aged joints. The project will lead to a number of papers, two PhD theses, and has already produced a number of conference papers, appendix I, {details of conference papers and reprints}. During the period of

the project Dr Crane and Dr Charles Lee of AFOSR have visited the laboratory at the University of Strathclyde and made very helpful inputs to the project. Professor Pethrick has visited the USA and contributed to the AFOSR review meeting at Long Beach {May 2000} and presented a paper at the AFOSR meeting in San Antonio Texas in December 2000.

The report is divided into three sections:-

- Studies of ageing of aluminium – epoxy –aluminium structures.
- Studies of ageing of CFRP –epoxy –CFRP structures.
- Initial investigation of boron fibre patches.

Studies Of Aluminium –Epoxy-Aluminium Structures

A previous study of ageing of joints made to commercial standards indicated that ageing at a temperature of 40°C or below over a three-year period was unlikely to produce significant ageing. This was contrary to the information available in the literature at that time. In the AFOSR funded study ageing was carried out at 50°C and 65°C to accelerate the effects of exposure at ambient temperature. The joints were fabricated using aircraft grade aluminium panels that had been etched and anodised using an industrial process. The sheets were bonded using a commercial adhesive and had strength characteristics that were identical with those used by BAe who supplied the materials. A large number of joints were made and all individually inspected prior to starting the study using high frequency dielectric measurements. Joints which failed the dielectric analysis were rejected either because of non- uniformity of the adhesive bond or other identifiable defect. The ageing study was conducted on three identical batches of bonds. From each batch was selected a set of reference samples and these were kept at constant temperature and not exposed to moisture. One set of joints was exposed to moisture at a constant temperature of 50°C. Joints were monitored on a frequent basis to determine the change in the dielectric signature with time and at selected intervals groups of joints were withdrawn for mechanical testing. Two types of mechanical test were carried out. Joints were cut to produce an overlapping section that was used for lap shear measurements. During fabrication strips of polytetrafluorothylene PTFE, were introduced into a group of joints and these were used to measure the joint strength from crack opening measurements. All mechanical measurements were made on at least five joints so as to ensure that sufficient measurements were made to represent a statistical average. Parallel studies were performed for a set of joints aged at 65°C. Isothermal ageing is the usual method of study of joints and difference in temperature related to different rates of the relevant processes but little appears to be known about the effects of thermal cycling on the ageing process. In order to establish whether thermal cycling has an effect on the process another set of samples were cycled between 50°C and 65°C on a monthly basis. All three sets of samples were prepared using the same materials and autoclave cured procedures. Representative samples of the joints were subjected to C-scan ultrasonic examination and were shown to be of good quality. The study of these samples was carried out over a period of two and a half years. The ageing of the dielectric samples was arranged to be about two months ahead of the mechanical samples hence allowing a better assessment of the best time to perform mechanical data.

As expected the rate of moisture uptake varied with temperature. It was also found that the thermal stepping of a joint did not produce data that was significantly different from the average of the two isothermal studies. This indicates that the effects

of moisture absorption appear to be independent of the route whereby the particular level is achieved. An unexpected result was the apparent high rate of corrosion that occurred at 50°C. Both the high temperature aged and cyclic aged samples showed a lower rate of corrosion. In all cases the water uptake occurred relatively rapidly initially and slowed down as the time was extended. The water absorbed lead to plasticization of the adhesive and a corresponding drop in the strength of the adhesive bond. The absorption of water was monitored in terms of an increase in the dielectric permittivity over the frequency range 1–200MHz and a corresponding increase in the loss. It is however evident that the moisture entering the joint was distributed between microvoids where it exhibited a signature of free water relaxing at approximately 12 GHz and bound water which relaxed in the lower frequency range and reflected a more hindered environment for the relaxation of the dipole. Because of corrosion of the outside of the aluminium joints it was not possible to use gravimetric measurements to access the extent of the moisture uptake in the joints. The data obtained from this study will be available in the thesis of Gordon Armstrong that will be submitted in May 2001 and will be available after that date on request.
The conclusions that emerged from this study were as follows:-

1) The initial stages of mechanical strength loss were paralleled by the observed increase in the permittivity of the joint associated with moisture ingress. This observation is consistent with the expectation from the literature on ageing that moisture has a major effect in determining mechanical loss. The dielectric data indicates that the moisture entering the adhesive is producing plasticisation.
2) The changes of the mechanical strength plotted against the change in the dielectric permittivity exhibits a similar shape for all three samples that were measured. This observation may be interpreted in terms of the effects of plasticisation and the modification of the interface due to corrosion - conversion of oxide to hydroxide.
3) The dielectric data showed the growth of a distinct feature in the MHz region that correlates with the growth of the oxide at the polymer –oxide interface. The appearance of this feature occurs at a time that reflects the point at which water changes the oxide to hydroxide. How the water moves to the interface is not clear at this time and may be either a consequence of either redistribution from the resin or through capillary action along the interface layer. The feature in the MHz frequency range however correlates closely with a marked drop in the strength of the adhesive bond. Inspection of the dielectric –mechanical data correlation indicated that the major drop in the strength could be associated with the corrosion of the interface.
4) The time domain data indicates the joints were initially of good quality. The peaks shift in proportion to the increase in the permittivity, reflecting the absorption of moisture by the adhesive. However, once the interface between the polymer and the oxide starts to develop a layer of hydroxide, additional peaks are observed in the time domain traces. The change in the structure of the time domain traces can be associated with changes in the thickness of the adhesive layer as a consequence of the thickening of the oxide layer on changing to hydroxide.
5) A detailed examination of the frequency dependent data indicated that once the oxide layer is formed there is evidence of a loss of bonding between the polymer and oxide and a drop of the permittivity associated with the creation of air voids within the structure.

The study has shown the potential of the dielectric method for the assessment of ageing on a simple joint structure. The study has further given insight into the relative

magnitude of the effects of plasticization and changes in the oxide polymer interface layer on the loss of strength of the adhesive bond.

Study Of Carbon Fibre Reinforced Plastic [CFRP]–Epoxy-CFRP Bonded Structures

Carbon fibres have a high intrinsic electrical conductivity and hence the potential of being used to guide electrical waves in a bonded structure. Previous studies have indicated the potential of looking at CFRP bonded structures using the dielectric method. In the present project the problem of understanding the way in which the orientation of the fibres in the composite next to the adhesive layer influence the electromagnetic propagation was addressed. It was shown that the best conditions for propagation were achieved with the carbon fibres orientated in the direction of the bond line. However, other orientations were observed to support propagation and it was even possible to observe reasonable signals provided that within the first three layers close to the bond line there was a set of fibres orientated in the bond direction. Fibres that are aligned either perpendicular or an angle (usually 45^{o}) to the bond line will disperse the signal and attenuate the response. However even for woven substrates it was possible in certain circumstances to observe signals that could be used to investigate the ageing of the joints. The problem of alignment of the fibres relative to the preferred direction for mechanical testing was examined. A compromise was obtained which produced good electrical signals and also allow satisfactory mechanical tests to be performed.

Two ageing studies were performed:-

1) Ageing in water – this was carried out at $65^{o}C$ and performed over an extended period. Two sets of samples were created using prepreg to create the composite and then to bond the substrates with a standard structural adhesive. The creation of the composites and the subsequent bonding was all carried out in an autoclave. The first set was found to obtain air voids and can be considered as a 'bad' set of joints. The defects were detected using C-Scan ultrasonic examination carried out at Wright Patterson Laboratories. The second set of joints produced appeared to be defect free by C-Scan examination. The initial strengths of the joints were found to be consistent with the expected values for that adhesive system. Ageing was carried out by exposure to 100% humidity. The increase in the weights of the composite and also the adhesive bond was investigated as a function of time and the effective diffusion coefficients into the structure determined. The values obtained were similar to those found in a previous study and were also consistent with the values in the literature. The gravimetric studies of water absorption were then used to assess the dielectric measurements.

   Analysis of the data.

   The time domain traces obtained from the composite panels and also the adhesive bonded structures were used to calculate the mean change in the dielectric permittivity. The frequency dependent data was also used to examine the distribution of the dipole relaxation across the accessible frequency range. Analysis of the data indicated that there is a good correlation between the change in the dielectric permittivity and the amount of water located in the adhesive layer. As indicated in the previous analysis of the model joint structure the electromagnetic wave is confined in the adhesive layer and hence the changes observed in the permittivity are related only to the moisture in the adhesive bond. Frequency dependent analysis indicates that there are two observable processes.

The first is associated with water dispersed in the adhesive and the location of the relaxation changes with the extent of hydration. This shift of relaxation frequency implies that the water molecules are changing the nature of their environment. An additional low frequency process can be associated with the hydration process liberating carrier ions and allowing ionic conductivity of the adhesive layer to be increased with the generation of Maxwell Wagner Sillers type processes. The latter are associated with the localised charge carriers (in this case ions) moving through the matrix. They are characteristic of an uncured system or one which has sufficient water molecules to exhibit ionic mobility. Such phenomena are observed before the hydration level reaches a level to sustain d.c. conductivity in the adhesive. A Kirkwood-Foss analysis of the higher frequency relaxation leads to a 'g' factor that is consistent with the process being observed being that of water molecule relaxation. The observed loss in mechanical strength in these composites is consistent with a plasticization mechanism.

2) Ageing in other solvent systems. A series of experiments were carried out on bonds that were exposed to a range of solvents:- sea water, deionised water, urea solution, propyleneglycol (deicing fluid), dichloromethane, butanone (paint strippers), hydraulic fluid and aviation fuel. These environments were considered to be typical of those found in a real situation. The objective of the study was to explore whether it was possible to determine the ingress of these fluids into the joint and also to establish what effect they have on the adhesive bond strength of the composite. The ageing study was carried out in a similar fashion to that described for the water study above with the exception of dichloromethane. Because of the high volatility and toxic nature of this chemical the ageing was carried out at room temperature (25^{o}C). Because the CFRP does not undergo corrosion it is possible to monitor changes in thickness and width of the structure with exposure. All the liquids initially are absorbed into the joint structure in a similar fashion, however the mass uptake for dichloromethane and butanone is much greater initially than for the other systems. This observation is consistent with the solvent characteristics of these liquids. The remainder of the liquids examined were absorbed into the joint in a pseudo Fickian type of behaviour which reflects the limited solubility of these materials in the polymer matrix. The greater the solvent uptake the greater the dimensional changes observed. In general the dielectric property changes reflect those which would be expected from the gravimetric analysis. However, for the case of dichloromethane and butanone there are significant differences in the variation of the mass and dielectric permittivity. These liquids are aggressive solvents which can produce significant plasticisation of the adhesive and cause extraction of material from the matrix. The change in the strength of the bonds is also consistent with a combination of plasticisation and void generation influencing the strength. The low values of the dielectric permittivity observed indicate that the gap between the fibre elements has become highly voided and that the average dielectric permittivity reflects a high level of incorporation of air in this part of the structure. The changes in the mechanical properties for the remainder of the solvents are consistent with the changes in the mechanical properties being primarily attributed to plasticisation. The behaviour of the aqueous based systems; water, deionised water and urea solutions are all similar and difficult to differentiate. Similarly, the de-icing fluid, hydraulic fluid and aviation fluid all exhibit characteristic of a poor solvent and limited ability to plasticise or extract/ dissolve the adhesive. This indicates that there is once more an approximate correlation of the change in the

dielectric property with mechanical strength, however for the weakly polar solvents this correlation is not as clear as in the case of water. These studies will be extended in the next project.

Boron Fibre Studies And Development Of The Dielectric Probe.

Boron fibre patches are used to repair damaged aircraft. Boron fibres unlike carbon fibres are none conducting and therefore the approach outlined for CFRP bonded structures is inappropriate for the NDE of these structures. The problem which is posed is to be able to 'look' through the boron fibre patch at the underlying aluminium oxide – adhesive interface. To be able to 'see' through the patch it is necessary to be able to perform measurements from one face only. The conventional electrodes used for cure monitoring of thermoset resins sense the change in the dielectric properties to a depth of approximately 100 microns from the electrodes. To be able to throw the electromagnetic field to the desired depth it is necessary to adjust the electrode spacing and the distribution of the field existing between the high and low electrodes
The study can be divided into two parts; a theoretical modelling study of possible configurations and the practical evaluation of the selected electrode configuration.

1. Theoretical modelling of possible probe structures. A finite element model was created which allowed mapping of the field distribution into a model dielectric media. The simplest model is to use an inter-digitated structure in which alternating electrodes are respectively held a potential and at earth. As expected this structure indicates that the field penetration depends on the spacing and the width of the electrodes. The typical field penetration obtained from such a structure with electrodes of equal width and spacing of the order of 0.1mm was of the order of 100 microns. This approach is not particularly efficient in generating fields into the dielectric media for a given electrode spacing. Other more complex patterns were also explored. Any surface moisture is likely to produce a thin, relatively conducting layer at the surface. To counter this possible problem guard electrodes at the low potential were created around the low electrode. Modelling indicated that this would decrease the influence of the surface layer.
   Finally a structure was explored which was based on a four electrode configuration where a second set of electrodes was inserted between the high and low electrodes and held at a potential midway between the high and low values. Analysis of the field generated by this configuration indicated that it produced a field that fell off less steeply with distance from the surface.
2. Experimental structures were created by lithographic development using etching of a photoresist coated copper clad polyimide. The process generated large area probes with dimensions typically 4 inches x 4 inches. The performance of these probes were evaluated in the laboratory using a pile of glass sheets. It was possible to explore the depth penetration by changing the number of sheets in the pile and using a base metal plate as reference. A series of boron fibre plates were also cured to allow exploration of the depth penetration characteristics. It was found that using the selected probe configuration it was possible to throw the field to a depth of several mm into the boron fibre composite. At the time this study was undertaken the thickness of the typical boron fibre patch was not known. It is now known that the typical patch is about 4 mm thick and hence the probe has the

capability of penetration down to the metal substrate. Ideally a probe should be designed which only allows the boron fibre to be probed and does not see the metal. Such a probe would allow the amount of moisture in the boron fibre composite to be assessed. Another probe structure would be created which allows the interfacial oxide layer to be probed. Comparison of the results form these two probe configurations would allow the dielectric nature of the aluminium oxide – boron fibre composite interface to be quantified. There was not time available for these studies to be undertaken.

Conclusions

The study undertaken with the support of the AFOSR grant has shown:-

1. That it is possible to correlate the changes in the mechanical properties of aluminium – epoxy – aluminium structural bonds with changes in the dielectric properties of the bonds. The ageing appears to divide into two regions; initial plasticisation of the adhesive layer and deterioration of the oxide interface due to conversion to hydroxide. The time domain data is consistent with changes in the bond line thickness once swelling of the adhesive occurs and when subsequent corrosion occurs.
2. In carbon fibre composite bonded structures there is a similar correlation between changes in the mechanical properties and the dielectric signature of the joint. However in this case the ageing is predominantly due to plasticisation of the adhesive layer and changes in the interface layer are more difficult to quantify. Studies using a very aggressive solvent, dichloromethane indicate that in addition to resin being extracted from the adhesive layer there is also the possibility of detachment of the adhesive from the fibre. Both effects lead to a dramatic lowering of the average dielectric constant and are indicative of a massive loss in mechanical strength.
3. Initial measurements using a probe designed to allow study of insulating substrates indicate that it is possible to generate a field to the depth required for the study of boron fibre patches and indicates that it is feasible to design probe systems which would allow exploration of this type of structure. The studies have indicate the potential of the dielectric method in being able to assist with the Non Destructive Examination of ageing aircraft structures. Further funding will be required to extent these studies to structures which are closer to those found in aircraft and to complete the generation of fundamental calibration data required for the interpretation of the changes in the dielectric signature which will be used to monitor ageing. An outline proposal has been created and will be refined in the near future.

Appendix

Papers which have arisen from the study.

1. *Non Destructive Analysis of adhesive joint structures - Dielectric measurements,* R. A. Pethrick, K. Jeffrey, E. Pollock, D. Hayward & S. Affrossman, ASE 88 The Third Adhesives, Surface Coatings & Encapsulants Exhibition & Conference Proceedings, 171-194 (1988).
2. *The application of dielectric relaxation measurements to the Non-Destructive Examination of adhesively bonded joint structures,* R. A. Pethrick, D. Hayward, S. Affrossman & P. Wilford, Nondestr. Test. Eval., Vol.6, 45-63, (1991).
3. *A method for the non-destructive investigation of adhesively bonded structures,* S. B. Joshi, D. Hayward, P. Wilford, S. Affrossman & R. A. Pethrick, The European Journal of Non-Destructive Testing 1(4), (1992), 190-199.
4. *Aspects of theoretical modelling for high frequency dielectric studies of adhesively bonded structures,* S. B. Joshi, R. A. Pethrick & D. Hayward, British Journal of NDT, Vol. 35, No. 3, (1993), 130-132.
5. *NDE of adhesive joints - high-frequency dielectric investigations adhesive-bonded structures,* W.M. Banks, D. Hayward, S.B. Joshi, Z.C. Li, K. Jeffrey and R.A. Pethrick, Insight, Vol. 37, No. 12, (1995), 964-968.
6. *Non-destructive examination of composite joint structures: a correlation of water absorption and high-frequency dielectric propagation,* W.M. Banks, F. Dumolin, D. Hayward, R.A. Pethrick and Zhi-Cheng Li, J. Phys. D: Appl. Phys. Vol. 29, No. 1, (1996), 233-239.
7. *Investigation of the hydration and dehydration of aluminium oxide-hydroxide using high frequency dielectric measurements between 300 kHz-3GHz,* R.A. Pethrick, D. Hayward, K. Jeffrey and S. Affrossman, Journal of Materials Science, 31, (1996), 2623-2629.
8. *Investigation of moisture ingress into adhesive bonded structures using high frequency dielectric analysis,* Z-C Li, D. Hayward, R. Gilmore and R.A. Pethrick, Journal of Materials Science 32, (1997), 879-886.
9. *Environmental ageing of adhesively-bonded joints. I. Dielectric studies,* S.B. Joshi, R.A. Pethrick, R. Gilmore, L.W. Yates and D. Hayward, J. Adhesion, Vol. 62, (1997), 281-315.
10. *Environmental ageing of adhesively-bonded joints. II. Mechanical studies,* S.B. Joshi, T.F. Gray, W.M. Banks, D. Hayward, R. Gilmore, L.W. Yates and R.A. Pethrick, J. Adhesion, Vol. 62, (1997), 317-335.
11. *High frequency electrical measurements of adhesive bonded structures - an investigation of model parallel plate waveguide structures,* Z-C Li, S. Joshi, D. Hayward, R. Gilmore and R.A. Pethrick, NDT&E International, Vol. 30, No. 3, (1997), 151-161.
12. *Application of dielectric analysis to the study of ageing in adhesive bonded structures,* R.A. Pethrick, S.B. Joshi, D. Hayward, Z-C Li, S. Halliday, W.M. Banks, R.

Gilmore, L.W. Yates, Materials Research Society Symposium Proceedings, Vol. 503 (1998), 69-74.

13. *Studies of water permeation into fibre reinforced composite structures,* E. Boinard, R.A. Pethrick and J. Dalzel-Job, Plastics, Rubber and Composites Processing and Applications, **27**, No.4 (1998) 206-211.

14. *Non-destructive testing of adhesive bonded structures using high-frequency dielectric measurements,* P. Boinard, D. Hayward, W.M. Banks, R.A. Pethrick, The Dielectrics Society 30th Annual Conference, "Dielectrics at High Frequencies: RF, Microwave and Optical", 12-14 April 1999, Darwin College, University of Kent.

15. *Influence of humidity on the durability of adhesively bonded aluminium composite structures,* S.T. Halliday, W.M. Banks, R.A. Pethrick, Journal of Materials: Design and Applications, Vol. 213 (1999), No.L1, 27-35.

16. *Dielectric and mechanical assessment of water ingress into carbon fibre composite materials,* R.A. Pethrick, D. Hayward, Z-C Li, W.M. Banks, F. Dumolin and S.T. Halliday, 'Composites for the Offshore Oil and Gas Industry', IMechE Seminar Publication (1999), 55-74.

17. *High frequency dielectric measurements and destructive testing for the investigation of water uptake in adhesively bonded joints,* G.S. Armstrong, R.A. Pethrick, W.M. Banks, Conference Proceedings (CD-ROM) - 12th Int. Conf. on Composite Materials (1999).

18. *Applications of dielectric techniques to the characterisation of adhesive bonded structures* R.A. Pethrick, S. Affrossman, R.F. Comrie, Z-C Li, G.S. Armstrong, K. Ivanova, S.T. Halliday, D. Hayward, W.M. Banks, Conference Proceedings - 7th Int. Conf. on Adhesion and Adhesives (1999), pp. 99-104.

19. *High-frequency dielectric spectroscopy as NDE technique for adhesively bonded composites structures,* P. Boinard, R.A. Pethrick, W.M. Banks, 'Recent Developments in Durability Analysis of Composites Systems', Proceedings of the 4th International Conference on Durability Analysis of Composite Systems - DURACOSYS '99, Brussels 11-14 July 1999.

20. *Dielectric spectroscopy as a non-destructive technique to assess water sorption in composite materials,* P. Boinard, E. Boinard, R.A. Pethrick, W.M. Banks, R.L. Crane, Science and Engineering of Composite Materials, Vol. 8, No.4 (1999) 175-179.

21. *Dielectric studies of adhesively bonded CFRP/epoxy/CFRP structures - design for ageing,* S.T. Halliday, W.M. Banks, R.A. Pethrick, Composites Science and Technology **60** (2000) 197-207.

22. *Dielectric studies of aging in aluminium epoxy adhesively bonded structures: design implications,* S.T. Halliday, W.M. Banks, R.A. Pethrick, Journal of Materials: Design and Applications (2000), Proceedings of IMechE, Part L, Vol. 213, 103-119.

23. *Non-destructive examination of adhesively bonded structures using dielectric techniques: review and some results,* S. Affrossman, W.M. Banks, D. Hayward, R.A. Pethrick, Proc. Instn. Mech. Engrs., Vol. 214 Part C (2000) 87-102.

24. *Non destructive evaluation of adhesively bonded composite structures using high frequency dielectric spectroscopy,*
P. Boinard, R.A. Pethrick, W.M. Banks, R.L. Crane, Journal of Materials Science, 35 (2000) 1331-1337.

25. *Dielectric and mechanical assessment of water ingress into carbon fibre composite materials,*
W.M. Banks, F. Dumolin, S.T. Halliday, D. Hayward, Z-C Li, R.A. Pethrick, Computers and Structures 76 (2000) 43-55.

26. *Bond inspection in composite structures,*
R. A. Pethrick. Comprehensive Composite Materials Vol 5: Test Methods, Non-Destructive Evaluation and Smart Materials, Elsevier Sciences Ltd., 359-392 (2000).

27. *Time domain reflection dielectric spectroscopy for durability assessment of adhesively bonded composite structures,*
P. Boinard, R.A. Pethrick, W.M. Banks, Plastics, Rubber and Composites 29, No.6 (2000) 288-293.